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Comparison of Deposition Methods of ZnO Thin Film on Flexible Substrate

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Abstract

This paper reports the effect of the different deposition methods towards the ZnO nanostructure crystal quality and film thickness on the polyimide substrate. The ZnO film has been deposited by using the spray pyrolysis technique, sol-gel and RF Sputtering. Different methods give a different nanostructure of the ZnO thin film. Sol gel methods, results of nanoflowers ZnO thin film with the thickness of thin film is 600nm. It also produces the best of the piezoelectric effect in term of electrical performance, which is 5.0 V and 12 MHz of frequency which is higher than other frequency obtained by spray pyrolysis and RF sputtering.

Keywords: *Zinc Oxide, Spray Pyrolysis, RF Sputtering, Sol gel, Piezoelectric*

1. Introduction

Zinc Oxide (ZnO) is the piezoelectric thin film materials which can be integrated into MEMS and microelectronic process. It holds a high potential in transducer and sensor applications. ZnO nanostructures have been widely used for sensing applications because of their high sensitivity to the chemical environment. Nanostructures have the advantage of a high surface area and electronic processes are strongly influenced by surface processes. It also can be used in surface acoustic wave due to its electrical and optical properties.

ZnO shows it is much easier to control the film stoichiometry, texture, and other properties [1]. This material has been widely exploited and results multiple form of crystal such as single grains, fibers, nanocrystal, nanorods, thick and thin film. There are various techniques in depositing the ZnO films which can divide by two categories 1) chemical process including chemical vapor deposition [2, 3] and sol-gel [4, 5] and 2) physical process, including sputtering [6,7], pulsed laser deposition [8-10], spray pyrolysis [11-12].

In this paper, we study the effect of the different method of the ZnO thin film deposition towards the electrical performance. This electrical performance leads to the piezoelectric effect which can be used further in sensor and transducer application. It also can stimulate a possible new method of fabricated SAW sensor

2. Research Method

The ZnO thin film was deposited by three different methods which are spray pyrolysis, sol gel method and RF sputtering. Before deposition process the polyimide need to be cleaned first by using alcohol swab. After that, check the polyimide surface by using the microscope.

First sample which denoted as A had been sprayed with spray pyrolysis technique therefore the precursor solution need to be prepared first. 0.3M Zinc Nitrate Hexahydrate ($Zn(NO_3)_2.6H_2O$) was dissolved in a deionized water. Then five drops of Acetic Acid were added to the spray solution to prevent the precipitation of $Zn(OH)_2$. The surface of a hot plate was covered with the aluminium foil and the substrates were placed at the center of the hot plate. The hot plate was heated to the temperature 300°. Next, the solution is sprayed onto the substrates by using the gas carrier such as an air compressor. The nozzle to substrate distance was fixed with 10cm while the spraying time was fixed at 15 minutes. After deposition, the ZnO films were annealed at a temperature of 150°C within 30 minutes in a vacuum.

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Sample B was prepared by sol gel method. First, dissolving Zinc Nitrate Hexahydrate in deionized water. Then, NaOH was added to the solution. The solution was magnetically stirred at 500rpm for 30 minutes at room temperature. A plain of polyimide substrate was placed in a petri dish. It was then soaked dropwise with the solution by using pipette, dried at 150°C in oven. Several repetitions of the above procedure with an occasional washing with distilled water to remove a by-product uniform coating of ZnO.

For sample C, RF sputtering was used to deposit the ZnO film on polyimide substrate. The Zinc target with purity 99.99% (250 mm diameter and 3mm thickness) was used for the deposition of the ZnO film with a 7cm distance from the substrate. The ratio of sputtering gas Ar to O_2 was 62:25 which is needed to fix the sputtering pressure to 10 mTorr. The RF power was 200 W and the substrate temperature was kept at room temperature.

Next, the surface morphology structure is analysed by using a field emission scanning electron microscope (FESEM Jeol JSM 76007) with an accelerating voltage 15keV. The thickness of ZnO films is measured by using surface profiler Alpha Step. The crystal structure of the films were studies using the PANalytical X-ray diffraction (XRD) working at 40 keV and 40mA. The diffraction patterns were obtained in the 2θ mode, which 2θ = 20°~ 70°. X-ray diffractograms were analyses using the Highscore system.

After depositing the ZnO thin film on the Polyimide being sandwiched with silver electrode as in Figure 1. The internal silver (Ag) electrode is shielded by the external Ag electrode because the structure contributes to avoid unexpected noise. This laminated structure to obtain the sensitivity, flexibility, and fatigue durability. The Polyimide separates the Ag electrodes not only because as a flexible substrate, but also as an insulating layer to avoid unexpected leakage of electric charges. By applying the voltage to the both electrodes, it will resemble as a parallel-plate capacitor and it is because of the deformation of piezo material.

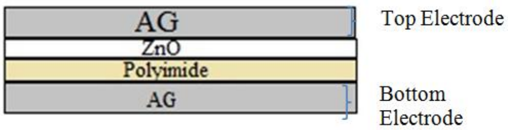


Figure 1. Schematic diagram of flexible piezoelectric thin film sensor with laminate structure

The frequency response of ZnO thin film can be measured by injecting a frequency to a circuit. Here, the frequency is injected into the circuit through a frequency generator to give the maximum voltage across the ZnO thin film. No power supply is needed in this experiment. Then, the frequency across the ZnO thin film is measured and explained in the next section.

3. Results and Analysis

After deposition, all the sampels were analyzed in term of crystal structure and electrical performance. This is important to study the characterization of ZnO towards flexible condition.

3.1. Surface Morphology and Crystal Structure Analysis

The prepared samples were characterized by FESEM and the purity of the sample was testing by energy dispersive spectroscopy (EDS).

ZnO films deposited from spray solution as shown in Figure 2(a) exhibit two different shapes which are flakes and nano particles in a range between 70 to 90nm. The structure is distributed evenly, but in different orientations.

The FESEM image of Figure 2(b) shows the different shapes of ZnO prepared sol-gel methods exhibited piles of flakes and cauliflower-like shape. The flakes are almost square and have different orientations. In general, it looks like nanoflower which is distributed evenly in range of 70-100nm. This ZnO covers up the whole surface of the substrate, but in certain condition such as at long durations ZnO films are cracked and peel off from the polyimide substrate because of the adhesiveness factor.

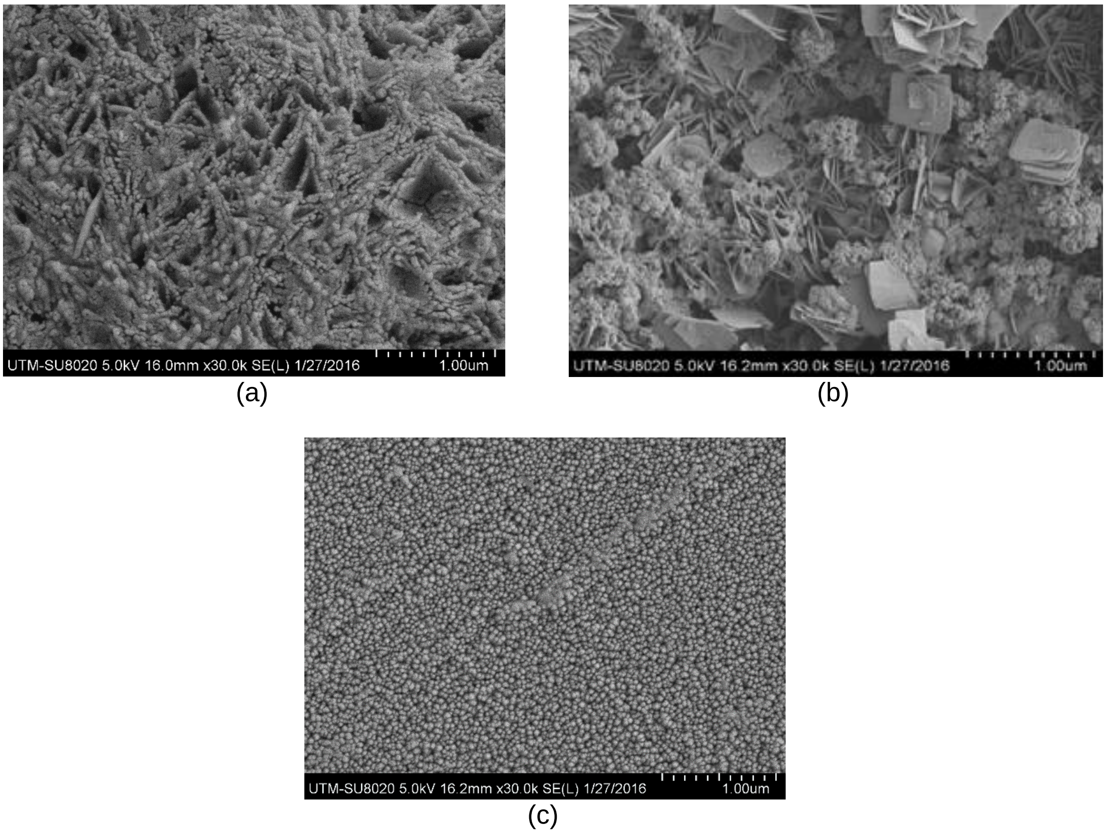


Figure 2. FESEM images of ZnO prepared by different methods; a) Spray Pyrolysis b) Sol gel and c) RF Sputtering

While for RF-Sputtering methods, the FESEM image results as in Figure 2(c), a compact nano particle array with the dimension of 20-30nm. The diameter of the nano-particles is uniform, which results in a homogeneous thickness of the film with a smooth surface. This ZnO nano grains are grown in C-axis. It shows that ZnO nanostructure is differing per methods for aqueous solution growth.

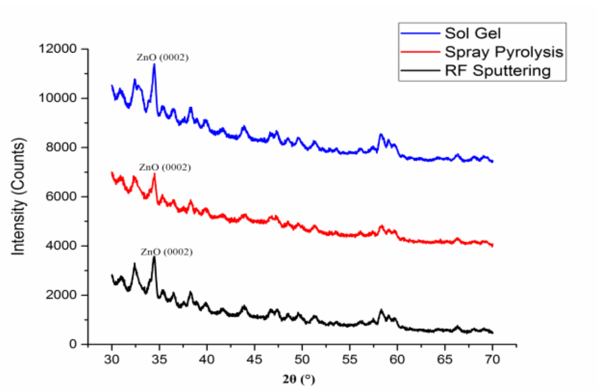
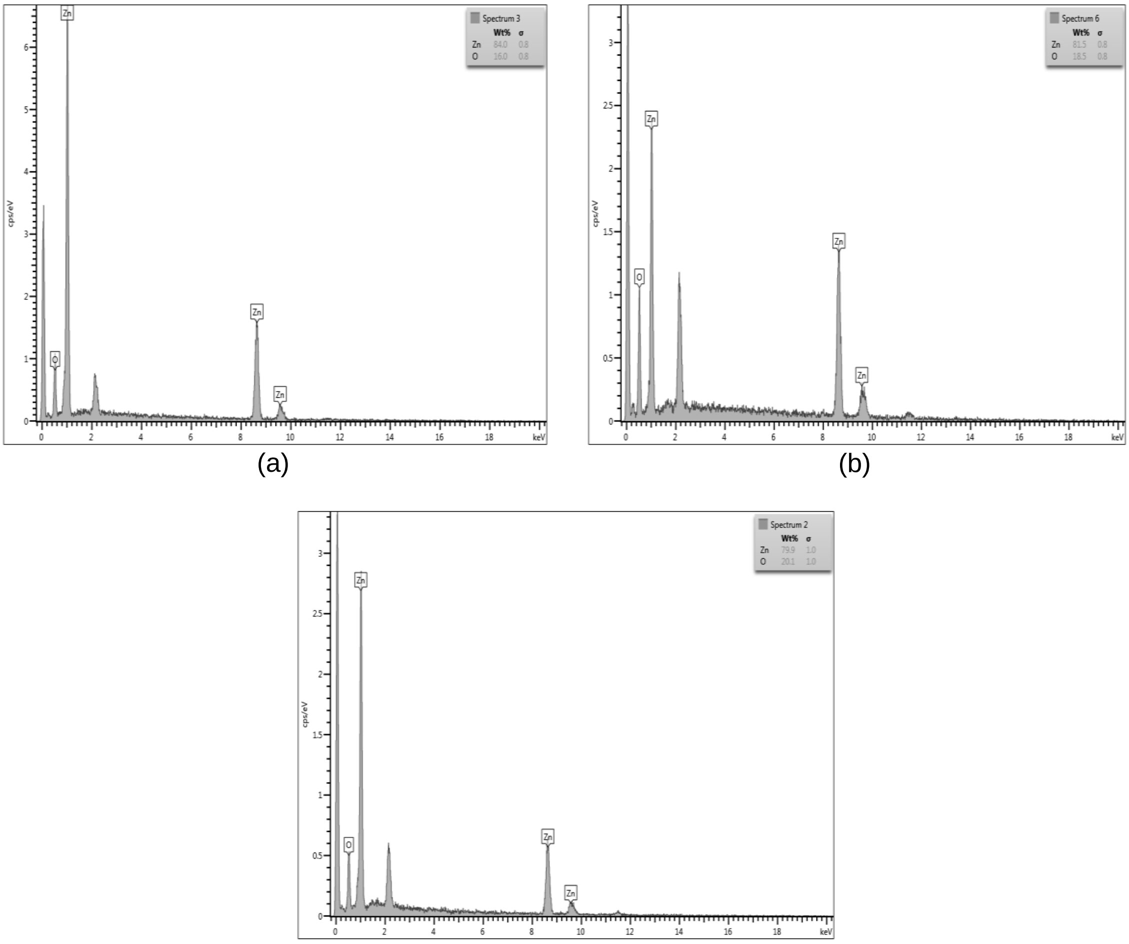


Figure 3. ZnO XRD prepared by different methods; A) Sol gel B) Spray Pyrolysis and C) RF Sputtering

Figure 3 shows the XRD patterns of the ZnO films on different methods. All films have a hexagonal wurtzite-type structure and the position of (0002) peak for all samples at 34.58°. The intensity of the peaks increase with calcination indicating increased crytallinity. Thick films of

ZnO indicate that the crystal quality becomes better with increasing the 0002 peak as mention by J. Zhou, et al., in [13]. As sol-gel give thicker ZnO thin film, the 0002 peak is higher then other methods.

The energy dispersive spectra of the samples obtained from the SEM-EDS analysis in Figure 4 show that the samples prepared by all three methods have pure ZnO phases.



(a) (b)

(c)

Figure 4. Energy dispersive Spectra of ZnO prepared by different methods; a) Spray Pyrolysis b) Sol gel and c) RF Sputtering

3.2. ZnO Thin Film towards the Electrical Performance

At rest position, the voltage is 0V. When the piece material sensor is bent, the mechanism is translated into a charged displacement. The positive charge is accumulated to one side while negative charge is accumulated to the other side and this cause the voltage to increase in ranged 0.5 - 5V. The displacement is changed temporarily and behaves like charging capacitor. As generated charge Q is proportional to the pressured area A, which is $Q = d_{33}$ PA, where P is pressure. The pressured area of the ZnO film increases on bending therefore the induced electric charge increase.

From Table 1, sample B gives a higher voltage peak to peak and frequency response. This is due to the thickness of ZnO thin film of Sample B is 600nm. The thickness of ZnO thin film for sample A and C are 300nm and 540nm respectively. Means that, the thickness affects the electrical performance. It also strongly shows that the thicker sample had contributed to the higher (0002) peaks as in Figure 3. This shown that the sample B which using the Sol-gel techniques give the higher frequency response.

Table 1. Electrical Performance towards Thin Film Thickness

Sample	Bent in (cm)	Voltage	Bent Out (cm)	Voltage	Frequency (MHz)
A	2.0	3.40	2.0	-3.50	5.80
	2.5	3.06	2.5	-3.00	5.00
	3.0	2.65	3.0	-2.78	4.86
B	2.0	5.37	2.0	-5.30	12.54
	2.5	5.00	2.5	-5.05	12.00
	3.0	4.69	3.0	-4.70	11.68
C	2.0	2.99	2.0	-3.00	3.30
	2.5	2.57	2.5	-2.60	3.00
	3.0	2.01	3.0	-2.00	2.70

Besides thickness, the grain size also contributes to the electrical performance. This because of it holds uniform nano-particles with almost the same diameter of grains. T.Li et.al in [14] had investigated the effect of the piezoelectric towards the ZnO micropillar size and said that grain size is considered one of the more important properties, particularly at high frequencies. As the aspect ratio increases the deflection of the nanostructure increase and leads to an enhancement in the output electrical potentials.

So, if the sample C, which is by using RF sputtering method during deposition is upgraded with the thickness value to the 540nm, the electrical performance will increase further higher than sample B. Sample C can be used in further research to stimulate a possible new method of fabricated a flexible SAW sensor. This is because the ZnO thin films that grown by RF sputtering had a strongly adhere.

4. Conclusion

The c-axis oriented ZnO thin film was grown on polyimide by three different methods which are spray pyrolysis, sol-gel and RF sputtering. The EDS analyses clearly indicate that highly pure ZnO is formed in the above methods. The size dependence of piezoelectric coefficients in ZnO thin films was investigated. In this experiment, it shown that sol gel gives the higher response to the electrical performance because of the higher thickness compare to others. The flexible ZnO thin film can be achieved and can be used further as a sensor. As the size of piezoelectric films structure is reduced to the nanoscale the conversion efficiency can be improved dramatically due to nanomaterials relatively.

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